Universal Attosecond Response to the Removal of an Electron

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When an electron is suddenly removed, a universal response of the system is shown to occur on an attosecond (10^{-18} s) time scale. During this response time, which lasts about 50 attoseconds, the density of the created hole changes in a characteristic way. Explicit examples are shown. The results are analyzed in terms of the eigenstates of the residual ion and related to the filling of the exchange-correlation hole associated with the electron in the ground state of the system by the remaining electrons.

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The electronic structure of atoms, molecules, clusters, and condensed matter has been the central subject of an enormous number of experimental and theoretical investigations in physics and chemistry, and more recently also in biology. Owing to the long-range interaction between electrons, their motion is rather correlated which often renders the understanding of the electronic structure difficult. Not surprisingly, many experimental and theoretical tools have been developed over the years to probe the system's electronic structure. A particularly appealing approach to study this structure is to remove a single electron from the system in a controlled way. Traditionally, this is done by photoelectron or photoemission spectroscopy [1,2] which provides detailed information on the binding energy and other properties the electron ejected by photoabsorption has had in the system. In the absence of electron correlation this information can be, at least in principle, computed accurately. Inclusion of electron correlation is, however, mandatory to be able to explain the experimental observations. Electron correlation gives rise to a whole zoo of phenomena [1–3].

In the present work we investigate the short-time response of the system to the sudden removal of an electron. We demonstrate that a remarkable response has already taken place before 50 attoseconds [(as); 1 as $= 10^{-18}$ s] have passed after the removal. The findings and their interpretation make clear that this response is universal for electronic systems, and it provides valuable information on the nature of electron correlation.

By suddenly removing an electron from a system in its ground state $|\Phi_0\rangle$, a state $|\Phi_i\rangle$ with one less electron is prepared which is not an eigenstate of the system. Nonstationary behavior will take place and the hole created in the system will migrate in space as a function of time. The density of this hole is simply given by the difference of the electron density $\rho_0(\vec{r}) = \langle\Phi_0|\hat{\rho}(\vec{r}, t)|\Phi_0\rangle$ in the ground state and the electron density $\rho_i(\vec{r}, t) = \langle\Phi_i|\hat{\rho}(\vec{r}, t)|\Phi_i\rangle$ in the initially prepared nonstationary state:

$$Q(\vec{r}, t) = \rho_0(\vec{r}) - \rho_i(\vec{r}, t). \tag{1}$$

The quantity $\hat{\rho}$ is the usual density operator [4]. $Q(\vec{r}, t)$ describes the density of the hole, or briefly *hole density,* at position $\vec{r}$ and time t. By construction the hole density is normalized at all times t.

As usual, the density operator is represented in a one-particle basis $\{\varphi_p(\vec{r})\}$, often called orbitals, $\hat{\rho}(\vec{r}, t) = \sum_{pq}\varphi^*_p(\vec{r})\varphi_q(\vec{r})a^+_p a_q$, where the a^+_p and a_q are the corresponding electron creation and annihilation operators [4]. Inserting this representation into Eq. (1) reveals the density character of Q:

$$Q(\vec{r}, t) = \sum_{pq}\varphi^*_p(\vec{r})\varphi_q(\vec{r})N_{pq}(t). \tag{2}$$

Here, $N_{pq}(t) = \langle\Phi_0|a^+_p a_q|\Phi_0\rangle - \langle\Phi_i|a^+_p(t)a_q(t)|\Phi_i\rangle$ which can be evaluated by inserting twice the unit operator $\sum_I|I\rangle\langle I|$, where $\{|I\rangle\}$ is the complete set of eigenstates of the ion created by the removal of an electron.

The migrating hole is described by the time-dependent elements $N_{pq}(t)$ of the matrix $\mathbf{N}(t)$ in the orbital basis $\{\varphi_p\}$. We can readily bring the hole density into an appealing form which is obtained by diagonalizing the matrix $\mathbf{N}(t)$. This leads to

$$Q(\vec{r}, t) = \sum_p|\tilde{\varphi}_p(\vec{r}, t)|^2\tilde{n}_p(t), \tag{3}$$

where the resulting eigenvalues $\tilde{n}_p(t)$ and the orthonormal eigenfunctions $\tilde{\varphi}_p(\vec{r}, t)$ depend on time. We call the $\tilde{\varphi}_p(\vec{r}, t)$ *natural charge orbitals* and the $\tilde{n}_p(t)$ are their *hole occupation numbers.* $\tilde{n}_p(t)$ informs us on which part of the charge of the hole is in the natural charge orbital $\tilde{\varphi}_p(\vec{r}, t)$ at time t. Because of the conservation of hole charge $\sum_p\tilde{n}_p(t) = 1$.

We have computed the migration of hole charges for many electronic systems and have found a similar short-time behavior. In Fig. 1 we show results on the hole occupation as a function of time for a noble gas atom (Kr), for a small molecule (CO_2), and for a more complex larger molecule (N-methyl acetamide CH_3-CO-NH-CH_3). It can be shown that the sudden removal of an electron leads to $\tilde{a}_i|\Phi_0\rangle$ and hence to the removal of an orbital from the ground state (see, e.g., [3] and references therein). The initial state has been prepared by removing an electron

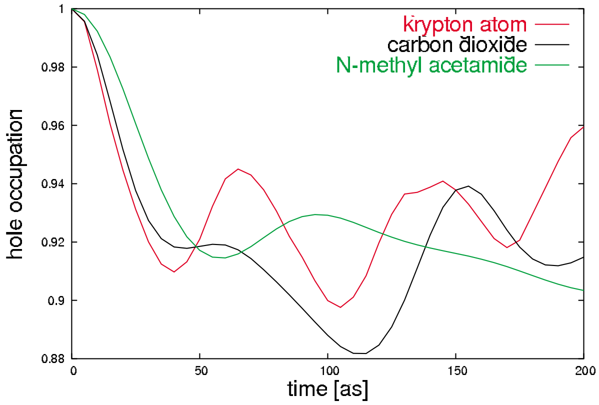

FIG. 1 (color online). Response of an atom (Kr), a small molecule (CO_2), and *N*-methyl acetamide (CH_3-CO-NH-CH_3) to the sudden removal of an electron. Shown is the hole occupation as a function of time on an attosecond time scale.

from an orbital $\tilde{\varphi}_i(\vec{r})$ [$= \tilde{\varphi}_i(\vec{r}, t = 0)$]. This implies that at time $t = 0$ the hole density is $Q(\vec{r}, 0) = |\tilde{\varphi}_i(\vec{r})|^2$; i.e., $\tilde{n}_i(t = 0) = 1$ and all other $\tilde{n}_p(t = 0) = 0$. As time proceeds, the natural charge orbital $\tilde{\varphi}_i(\vec{r}, t)$ varies and with it its occupation number $\tilde{n}_i(t)$. For convenience, we have chosen $\tilde{\varphi}_i(\vec{r})$ to be a Hartree-Fock orbital of the respective system in its ground state. The universality of the effect we discuss in this work does not depend on this choice; we could have chosen orbitals from density functional theory [5] or other functions. Nevertheless, we mention here that the present choice does have some conceptual advantages [6]. The curves in Fig. 1 are for initial ionization out of the $2p$ orbital of Kr, the $1\pi_u$ orbital of CO_2, and the 3π orbital of CH_3-CO-NH-CH_3.

In spite of the vastly different nature of the systems studied, Fig. 1 shows at short times up to 50 as a fast monotonously decreasing hole occupation for all systems. After about that time, a different charge migration mechanism sets in and the hole occupation starts to oscillate with characteristics specific for each system. Because of the conservation of hole charge, the hole occupation of our initially ionized orbital $\tilde{\varphi}_i(\vec{r}, t)$ continuously flows to other natural charge orbitals of the system as time proceeds. The changes in real space of the hole density $Q(\vec{r}, t)$ during the first 50 as are even more pronounced than those anticipated by inspection of Fig. 1 (see below). The reason is that Fig. 1 shows the hole occupation of $\tilde{\varphi}_i(\vec{r}, t)$, but this natural charge orbital deforms as well as a function of time and, in particular, other orbitals of different spatial topology and location become populated, too.

Before proceeding with the analysis of the charge migration on the attosecond time scale, we discuss briefly a few computational details. The hole density $Q(\vec{r}, t)$ has been computed by using *ab initio* methods only. These methods have been in part newly developed for this purpose. We do not go into details here. We just mention that the hole density in Eq. (2) is evaluated as indicated in the text below this equation. To this end, we have computed a very large number of eigenstates $|I\rangle$ and eigenenergies E_I of the ion created by the removal of an electron and evaluated the quantity

$$N_{pq}(t) - N_{pq}(0) = \sum_{IJ} \langle\Phi_i|I\rangle\langle I|a_p^+ a_q|J\rangle\langle J|\Phi_i\rangle\{1 - \cos[(E_I - E_J)t]\}. \qquad (4)$$

For more details, see Ref. [7] and references therein.

As an example we show in the upper panel of Fig. 2 the calculated ionization spectrum of CO_2. Each eigenstate $|I\rangle$ is represented by a vertical line at the respective ionization energy which is given by $E_I - E_0$, where E_0 is the ground state energy of the system. Those eigenstates which are populated by preparing the initial nonstationary state $|\Phi_i\rangle$ discussed above are shown in the figure in black. The heights of the corresponding vertical lines are given by $|\langle I|\Phi_i\rangle|^2$. Analogously, a subset of the other lines seen in

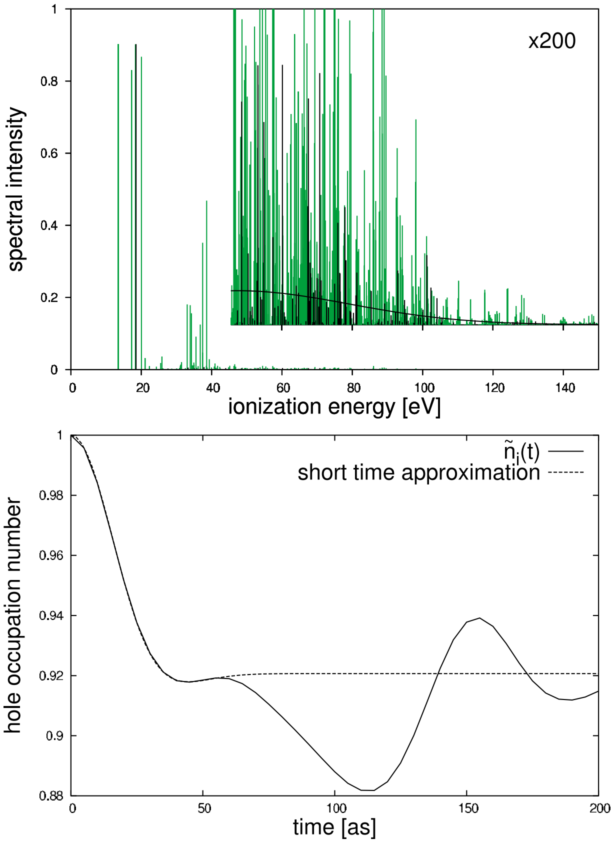

FIG. 2 (color online). Upper panel: ionization spectrum of CO_2. Each vertical line is associated with an eigenstate of the ion. At high energy the spectrum consists of numerous weak lines. The inset shows these lines on an enlarged scale. The lines in black correspond to the eigenstates contributing to the nonstationary state prepared (see the text). Lower panel: the hole occupation of CO_2 as a function of time (as in Fig. 1) and the result of the short-time approximation in Eq. (5) with $A = 0.079$, $\Omega = 44.091$/fs, and $\Delta = 49.151$/fs (dashed line).

the figure (the gray ones) would play a role if the initial state is prepared by removing an electron from another orbital of CO_2. From Fig. 2 we see that the initially prepared state approximates quite well a single eigenstate $|I\rangle$, namely, that seen just below 20 eV. The height of this line is ≈ 0.9. In other words, since $|\Phi_i\rangle$ is normalized and hence $\sum_I |\langle I|\Phi_i\rangle|^2 = 1$, only a small fraction $(1 - 0.9 = 0.1)$ of the spectral intensity is left for all other eigenstates contributing to $|\Phi_i\rangle$. This fraction is found by the calculation to be divided among many eigenstates. Indeed, the respective black vertical lines in the spectrum are tiny and can hardly be seen. Their existence becomes evident once the spectral intensity distribution is magnified as seen in the inset of Fig. 2.

We stress here that the many initially weakly populated high-energy eigenstates are responsible for the short-time response to the removal of an electron. In *all* examples studied including larger molecules where the spectra are much more intricate than for CO_2 discussed above, the short-time response disappears if we discard the weakly populated high-energy eigenstates. To further facilitate this central point and, at the same time, to derive an estimate for the short-time response, we introduce in the following a simple model. In this model we consider a single main eigenstate $|I_0\rangle$ which carries most of the spectral intensity $|\langle I_0|\Phi_i\rangle|^2$ and a dense set of weakly populated eigenstates $|I\rangle$ located at higher energy. Furthermore, we assume that out of all elements $N_{pq}(t)$ in Eq. (2), the element $N_{ii}(t)$ is the dominating one at short times (this is, of course, absolutely true at $t = 0$). At last, we take the overlaps $|\langle I|\Phi_i\rangle|^2$ to follow a Gaussian distribution $a\exp[-(E_I - \bar{E})^2/(4\Delta^2)]$, estimate $\langle I|a_i a_i^+|J\rangle$ by $\langle I|a_i|\Phi_0\rangle\langle\Phi_0|a_i^+|J\rangle$, and replace the sum over the states I and J in Eq. (4) by integrations over the energies E_I and E_J. The result reads

$$\tilde{n}_i(t) = 1 - A[1 - \cos(\Omega t)\exp(-\Delta^2 t^2)], \qquad (5)$$

where $A = 2\sqrt{\pi}|\langle I_0|\Phi_i\rangle|^2 a\Delta$ and $\Omega = \bar{E} - E_{I_0}$. When fitted to the full numerical result, this short-time approximation to the hole occupation reproduces the full result excellently up to 50 as. An example is shown in the lower panel of Fig. 2 for the case of CO_2. Although the model is crude, it explains the short-time response. The reason for this success lies in the fact that many states contribute collectively and, therefore, the details of a contributing individual state are not relevant as long as the average behavior is correctly described.

Let us now turn to what is, in our view, the key to the understanding of the attosecond response. In Fig. 3 we show for CO_2 the hole density itself in space as a function of time from $t = 0$ up to 45 as. Because of the cylindrical symmetry of this molecule it is convenient to depict the radial dependence of $Q(\vec{r}, t)$. This is achieved by integrating $Q(\vec{r}, t)$ over the remaining two coordinates. We denote the radial dependence of the hole density by $Q(x, t)$. At $t = 0$ the hole density has a bell-like shape. As time proceeds electrons flow into the wings of the hole density distribution (remember that by definition $Q > 0$ means a hole and $Q < 0$ means the absence of a hole, i.e., the presence of electrons). At the same time the hole becomes more localized and its central part grows. During the first 45 as the maximum of $Q(x, t)$, i.e., $Q(0, t)$, grows by more than 40%; actually most of this increase takes place during the first 30 as, which is consistent with the behavior of the hole occupation in Figs. 1 and 2.

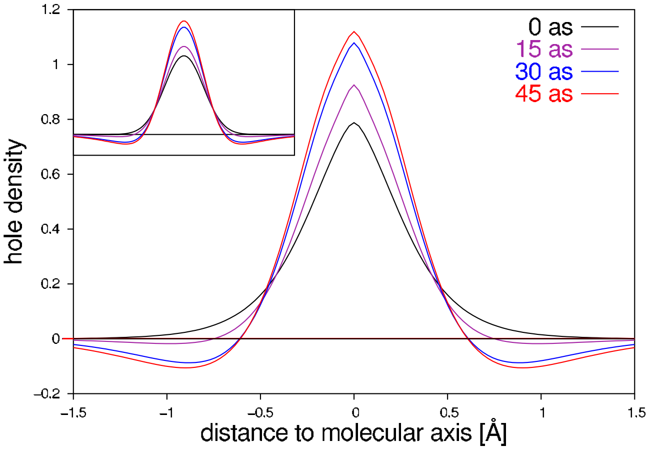

FIG. 3 (color online). The density of the hole in space as a function of the first 45 as. The results are for CO_2 and correspond to the hole in Figs. 1 and 2. Depicted is the radial hole density (see the text). The inset shows the result of Eq. (6) where the initially created hole and the exchange-correlation hole function are approximated by normalized Gaussians $[|\tilde{\varphi}_i(x)|^2 \sim \exp(-1.8\ \mathrm{au}^{-2}x^2)$, $h(x) \sim \exp(-0.25\ \mathrm{au}^{-2}x^2)$, and $\alpha = 0.4]$.

To interpret the results let us first discuss the situation in the ground state of the system and consider the pair distribution function $g(\vec{r})$. This function is the distribution of electrons, on the average, about any electron. It is well-known that due to exchange and correlation $g(\vec{r})$ is reduced in the neighborhood of $\vec{r} = 0$; i.e., the electron charge is depleted in the vicinity of the electron [8]. This reduction leads to what is generally called the exchange-correlation hole [5,8]. This hole moves with the electron. To a particular electron even in a so-called homogeneous electron gas, the system is not uniform at all, since other electrons are not likely to venture near to it as they are to other points. Obviously, when an electron is suddenly removed from the ground state, its exchange-correlation hole has no reason to be sustained and will be filled by electrons as time proceeds. This is exactly what leads to the behavior seen in Fig. 3.

The electron has been removed from the distribution $|\tilde{\varphi}_i(\vec{r})|^2$, and we have to compute the exchange-correlation hole this distribution has in the ground state. To this end we first need the corresponding "pair" distribution function $\tilde{g}(\vec{r})$ which is the probability to find an electron in $\vec{r}$ while the other electron has the distribution $|\tilde{\varphi}_i(\vec{r})|^2$. The usual function $g(\vec{r})$ discussed above is obtained from the two-particle density $\gamma(\vec{r}, \vec{r}')$ assuming that one particle is at $\vec{r}' = 0$, i.e., from $g(\vec{r}) \sim \int \gamma(\vec{r}, \vec{r}')\delta(\vec{r}')d\vec{r}'$ [8]. Analogously, $\tilde{g}(\vec{r})$ follows from $\gamma(\vec{r}, \vec{r}')$ assuming that one particle has the distribution $|\tilde{\varphi}_i(\vec{r}')|^2$, i.e., $\tilde{g}(\vec{r}) \sim \int \gamma(\vec{r}, \vec{r}')|\tilde{\varphi}_i(\vec{r}')|^2 d\vec{r}'$. To obtain the exchange-correlation hole function $h(\vec{r})$ we now have to subtract $\tilde{g}(\vec{r})\rho_0(\vec{r})$ from $\rho_0(\vec{r})$, where $\rho_0(\vec{r})$ is the electron density in the ground state [8]. After the sudden removal of the electron at $t = 0$ the exchange-correlation hole of that electron can be filled by the remaining electrons. Since one can expect that the neighboring electrons will move in first, this process is fast and we assume that its time dependence is dictated by that of the depletion of the hole occupation, see Fig. 2 and Eq. (5), i.e., by a term proportional to $1 - \tilde{n}_i(t)$:

$$Q(\vec{r}, t) = c(t)\{|\tilde{\varphi}_i(\vec{r})|^2 - \alpha h(\vec{r})[1 - \cos(\Omega t) \times \exp(-\Delta^2 t^2)]\}. \tag{6}$$

α is the proportionality constant and $c(t)$ is a trivial time-dependent normalization constant introduced to ensure that the hole density is normalized.

Let us now return to the radial hole density distribution in Fig. 3 and apply the ansatz (6). We choose the one-dimensional functions $|\tilde{\varphi}_i(x)|^2$ and $h(x)$ to be simple Gaussians and take the other quantities from the short-time approximation of $\tilde{n}_i(t)$ used in Fig. 2. Since all quantities except that of $h(x)$ are given, one can obtain the Gaussian approximating $h(x)$ from a fit to the *ab initio* data in Fig. 3. The result for $Q(x, t)$ using Eq. (6) is depicted in the inset of Fig. 3. In spite of the simplifying assumptions, the agreement with the *ab initio* data is remarkable.

In conclusion, using many-body *ab initio* techniques, the hole density created by suddenly removing an electron has been calculated as a function of space and time. A universal fast response of the system takes place after this removal and is essentially completed within 50 as. The well-known exchange-correlation hole associated with an electron in the ground state of the system is filled by neighboring electrons as a function of time once the electron is removed. To correctly describe this flow of charge, a large number of eigenstates of the ionized system must be included in the theoretical description and are populated in reality by a sudden removal of an electron. The *ab initio* calculations are relatively cumbersome but have the advantage that no essential approximations are involved. Apart from the information obtained on the migration of the created hole, information also on the exchange-correlation hole can be extracted from the present calculations.

Finally, we briefly touch upon possible experimental realizations to investigate the above findings. To prepare the initial state an electron must be suddenly removed from the system. In principle, this can be accomplished by ionizing the system with a high-energy photon. Collisions with highly charged relativistic ions provide another possibility. Annihilation of an electron by a positron is also sudden and sounds attractive, at least in principle. To measure the short-time response, and the charge migration in general, it would be desirable to use time-resolved pump-probe techniques. Traditionally, these techniques operate in the femtosecond (10^{-15} s) regime [9]. More recently, however, subfemtosecond pulses have been utilized for pump-probe experiments [10,11]. Although the achieved resolution (≈ 200 as) is currently too low to study the short-time response investigated in this work, the field of ultrashort light pulses is developing fast and the desired resolution could be achieved some day. Another potential approach to generate ultrashort pulses is by highly charged relativistic ions. Such ions can generate subattosecond electromagnetic pulses which can be interpreted as a field of equivalent photons [12].

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